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BY:

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Atsushi Ueda et al. :
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Title: Non-aqueous Electrolyte Secondary Battery

TRANSMITTAL OF VERIFIED TRANSLATION OF PRIORITY DOCUMENT

Submitted herewith is a verified translation of Japanese Patent Application No. 2001-019556, filed in Japan on January 29, 2001, for which the benefit of foreign priority was previously requested on January 28, 2002. This submission completes the record in accordance with 37 C.F.R. § 1.55(a)(4).

Respectfully submitted,

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This 14th day of May 2004

Yasuhiro Yamazoe

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(Translation)

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[TITLE OF DOCUMENT] Specification 1

[TITLE OF DOCUMENT] Drawing 1

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(Translation)

[DOCUMENT NAME] Abstract

[ABSTRACT]

[OBJECTIVE] To provide a non-aqueous electrolyte secondary battery having excellent charge and discharge characteristics at a low temperature and showing satisfactory charge and discharge characteristics even after the battery is stood still under a high temperature condition over a period of time.

[SOLVING MEANS] Where a cyclic carboxylic acid ester exerting high conductivity under a low temperature condition is used as an electrolyte, a cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond is contained therein to suppress reductive decomposition of the cyclic carboxylic acid ester, and a cyclic carbonic acid ester having no unsaturated bond is further contained therein to suppress excessive polymerization reaction of the cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond under a high temperature condition.

[SELECTED DRAWING] FIG. 1

2001-019556

(Translation)

[DOCUMENT NAME] Specification

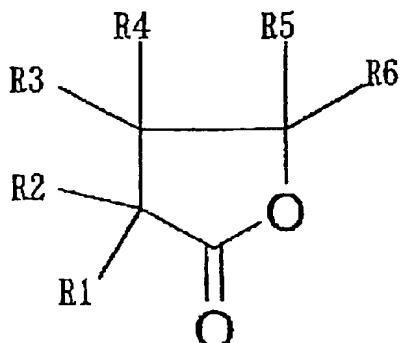
[TITLE OF THE INVENTION] NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY

[CLAIMS]

[Claim 1] A non-aqueous electrolyte secondary battery using an electrolyte dissolving a solute in a non-aqueous solvent comprising a cyclic carboxylic acid ester, a cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond and a cyclic carbonic acid ester having no unsaturated bond.

[Claim 2] The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said cyclic carboxylic acid ester is at least one selected from the group consisting of γ -butyrolactone and a derivative of γ -butyrolactone represented by the formula (1) (where R^1 to R^6 are, independently, a hydrogen atom, a halogen atom, an alkyl group having 1 to 6 carbon atoms, or an acetyl group having 1 to 6 carbon atoms).

[Formula 1]



[Claim 3] The non-aqueous electrolyte secondary battery in

accordance with Claim 2, wherein said derivative of γ -butyrolactone is γ -valerolactone.

[Claim 4] The non-aqueous electrolyte secondary battery in accordance with Claim 1, wherein said cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond is at least one selected from the group consisting of vinylene carbonate, vinylethylene carbonate and divinylethylene carbonate.

[Claim 5] The non-aqueous electrolyte secondary battery in accordance with Claim 1, wherein said cyclic carbonic acid ester having no unsaturated bond is at least one selected from the group consisting of propylene carbonate, ethylene carbonate and butylene carbonate.

[Claim 6] The non-aqueous electrolyte secondary battery in accordance with Claim 1, wherein said cyclic carboxylic acid ester is at least one selected from the group consisting of γ -butyrolactone and γ -valerolactone, said cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond is at least one selected from the group consisting of vinylene carbonate, vinylethylene carbonate and divinylethylene carbonate, and said cyclic carbonic acid ester having no unsaturated bond is at least one selected from the group consisting of propylene carbonate and ethylene carbonate.

[Claim 7] The non-aqueous electrolyte secondary battery in accordance with Claim 1, wherein said electrolyte comprises a linear carbonic acid ester.

[Claim 8] The non-aqueous electrolyte secondary battery in accordance with Claim 6, wherein said linear carbonic acid ester is at least one selected from the group consisting of dimethyl carbonate, ethylmethyl carbonate and diethyl carbonate.

[Claim 9] The non-aqueous electrolyte secondary battery in accordance with Claim 1, wherein said electrolyte comprises a glime.

[Claim 10] The non-aqueous electrolyte secondary battery in accordance with Claim 9, wherein said glime is at least one selected from the group consisting of diglime, triglime and tetraglime.

[Claim 11] The non-aqueous electrolyte secondary battery in accordance with any one of Claims 1 to 9, wherein a positive electrode active material is a lithium-containing transition metal oxide and a negative electrode material is graphite.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a non-aqueous electrolyte secondary battery. More specifically, the present invention relates to improvement in a solvent of a non-aqueous electrolyte, aimed particularly at improving charge and discharge characteristics under a low temperature condition.

[0002]

[Prior Art]

There has recently been a rapid advancement in

realization of small, lightweight and cordless electronic appliances such as personal computers and portable telephones, leading to a high demand for secondary batteries having a high energy density as power sources for these appliances. Among them, a non-aqueous electrolyte secondary battery containing lithium as an active material has been expected greatly to be a battery having a high voltage and high energy density. This battery conventionally comprised a negative electrode using metal lithium and a positive electrode using molybdenum disulfide, manganese dioxide, vanadium pentoxide or the like, to be a 3V-level battery.

[0003]

In the case that metal lithium is used for the negative electrode, however, there was a problem that dendritic lithium deposits on the electrode plate during charging and is accumulated thereon as the charging and discharging are repeated, the accumulated dendritic lithium being isolated, floating in the electrolyte and coming into contact with the positive electrode to incur a minor short. This resulted in a short cycle life as charge and discharge efficiency of the battery became less than 100 %. And there was another problem in terms of safety since dendritic lithium had a large surface area and thus had the high reaction activity.

[0004]

In order to solve these problems, vigorous studies have been done in recent years on a lithium-ion secondary

battery in which a carbon material is used for the negative electrode in place of metal lithium, and a lithium-containing transition metal oxide having a 4V-level potential against lithium such as LiCoO_2 , LiNiO_2 or LiMn_2O_4 , is used for the positive electrode, the battery having already been commercialized. In this battery, lithium is in the state of being absorbed as ions in the carbon material in the negative electrode. This prevents the deposition of dendritic lithium, which was observed on the conventional negative electrode using metal lithium, and thus enables the battery to ensure extremely high reliability in safety.

[0005]

As thus described, the characteristics of the positive electrode and the negative electrode are of importance in a non-aqueous electrolyte secondary battery, particularly in a lithium-ion secondary battery. And further, if satisfactory characteristics are to be obtained, the characteristic of a non-aqueous electrolyte transferring lithium ions is also of importance. A non-aqueous solvent composing this non-aqueous electrolyte is usually a combination of a solvent having a large dielectric constant which facilitates dissolution of an electrolyte and a solvent having low viscosity. The reason for the combination is as follows. The solvent having a large dielectric constant has high viscosity and thus transfers ions very slowly. Then, a solvent having low viscosity is also used so as to enhance capability of transferring ions. For example,

a cyclic carbonic acid ester, which is the solvent having a large dielectric constant, such as ethylene carbonate (EC), and a linear carbonic acid ester, which is the solvent having low viscosity, such as dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethylmethyl carbonate (EMC) are mixed to obtain an electrolyte having high conductivity, which has hitherto been in general use. Because EC has a solidifying point of as high as around 38 °C, when it is singly used, the solidifying point may go down to around 0 °C at the lowest even with the consideration of the freezing point depression due to the solute dissolved therein. As described above, therefore, low temperature characteristics are ensured by mixing with the solvent having low viscosity and a low solidifying point. However, even the mixed solvent cannot ensure sufficient low temperature characteristics since no small effect of EC on the low temperature characteristics remains.

[0006]

Thereupon, an electrolyte using a lactone-type solvent, which is a cyclic carboxylic acid ester, has been proposed (in Japanese Laid-Open Patent Publication No. Hei 11-097062). This is a very preferable solvent for the lithium-ion secondary battery as having a solidifying point of as low as -45 °C while having a large dielectric constant.

[0007]

[Problem That the Invention Is to Solve]

However, γ -butyrolactone (GBL), one of lactone-type

solvents, has a drawback of being prone to reductively decomposed on the negative electrode, which leads to generation of a large amount of decomposition gas in the battery. In order to suppress the reductive decomposition of GBL on the negative electrode, a battery has been studied in which vinylene carbonate (VC), known as an additive to form a film on a negative electrode, is added to an electrolyte containing GBL. But this battery exhibits significant deterioration in charge and discharge characteristics when the battery is stood still under a high temperature condition over a period of time. This is presumably because the decomposition of VC on the negative electrode is accelerated by heat to form an excessive film on the negative electrode. As a result, smooth intercalation and deintercalation of lithium ions into and from the negative electrode is prevented, resulting in significant deterioration of charge and discharge characteristics of the battery after exposure of the battery under a high temperature over a period of time.

[0008]

The present invention is to provide a non-aqueous electrolyte secondary battery in which the above-mentioned problems are solved, having excellent charge and discharge characteristics, particularly at a low temperature, and showing satisfactory charge and discharge characteristics even after being exposed to a high temperature over a period of time.

[0009]

[Means for Solving the Problem]

As trying to solve the above-mentioned problems, the inventors of the present invention diligently studied, to find that by making a cyclic carbonic acid ester having no unsaturated bond contained in an electrolyte comprising a cyclic carboxylic acid ester represented by a lactone-type solvent and a cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond, obtained is a non-aqueous electrolyte having excellent charge and discharge characteristics at a low temperature and exerting satisfactory charge and discharge characteristics even after the battery is stood still under a high temperature condition over a period of time. The following are the reasons for the excellent battery characteristics of the above-mentioned non-aqueous electrolyte. The cyclic carbonic acid ester having carbon-carbon unsaturated bond occurs a chain polymerization reaction successively on the negative electrode, as the unsaturated bond part is highly prone to be polymerized, and rapidly forms a close and strong film on the negative electrode. This film is formed on the negative electrode and serves as a physical barrier inhibiting intercalation of solvent molecules around lithium ions in the negative electrode, suppressing the reductive decomposition of the cyclic carboxylic acid ester on the negative electrode. However, in the case that a battery, produced using the electrolyte comprising a cyclic carboxylic acid ester and a cyclic carbonic acid ester having at least one carbon-carbon

unsaturated bond, is stood still under a high temperature condition over a period of time, the decomposition of the cyclic carbonic acid ester having carbon-carbon unsaturated bond on the negative electrode is accelerated by heat, forming an excessive film on the negative electrode. As a result, lithium ions are not smoothly intercalated into and deintercalated from the negative electrode, thereby raising a problem that the charge and discharge characteristics of the battery are significantly deteriorated. Then, further containment of the cyclic carbonic acid ester having no carbon-carbon unsaturated bond in the electrolyte allows suppression of the excessive polymerization of the cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond under a high temperature condition. A cyclic carbonic acid ester having no carbon-carbon unsaturated bond such as EC or PC is also reductively decomposed and forms a film derived from the decomposed product on the negative electrode, like a cyclic carbonic acid ester having a carbon-carbon unsaturated bond such as VC. However, since PC and EC have no carbon-carbon unsaturated bond, they forms the film much slower than VC or the like which forms a film by polymerization of the unsaturated bond. In the case that PC or EC is bonded in the halfway through the polymerization reaction of VC, the reactivity of that part becomes very low, which suppresses the excessive polymerization of VC under a high temperature condition. This results in realization of a battery having

satisfactory charge and discharge characteristics even after exposure of the battery to a high temperature over a period of time.

[0010]

[Mode for Embodying the Invention]

In the following, detailed embodiments of the present invention are described. The non-aqueous electrolyte secondary battery in accordance with the present invention comprises therein a cyclic carboxylic acid ester having a large dielectric constant excellent charge and discharge characteristics under a low temperature condition, a cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond and a cyclic carbonic acid ester having no unsaturated bond.

[0011]

The exemplary cyclic carboxylic acid esters may include γ -butyrolactone, γ -valerolactone, α -acetyl- γ -butyrolactone, α -methyl- γ -butyrolactone, β -methyl- γ -butyrolactone, α -angelica lactone, α -methylene- γ -butyrolactone, γ -hexanolactone, γ -nonanolactone, γ -octanolactone and γ -methyl- γ -decanolactone.

[0012]

The exemplary cyclic carbonic acid esters having at least one carbon-carbon unsaturated bond may include vinylene carbonate (VC), 3-methylvinylene carbonate, 3,4-dimethylvinylene carbonate, 3-ethylvinylene carbonate, 3,4-

diethylvinylene carbonate, 3-propylvinylene carbonate, 3,4-dipropylvinylene carbonate, 3-phenylvinylene carbonate, 3,4-diphenylvinylene carbonate, vinylethylene carbonate (VEC) and divinylethylene carbonate (DVEC). These compounds may partially be replaced with fluorine atoms.

[0013]

The exemplary cyclic carbonic acid esters having no unsaturated bond may include propylene carbonate (PC), ethylene carbonate (EC) and butylene carbonate (BC). These compounds may partially be replaced with fluorine atoms.

[0014]

The content of the cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond is preferably 0.5-20 % by volume, and the content of the cyclic carbonic acid ester having no unsaturated bond is preferably 0.1-20 % by volume.

[0015]

By containing a linear carbonic acid ester in the electrolyte, the viscosity thereof is lowered, enabling further improvement in the charge and discharge characteristics at a low temperature. The exemplary linear carbonic acid esters may include dimethyl carbonate (DMC), ethylmethyl carbonate (EMC) and diethyl carbonate (DEC).

[0016]

The electrolyte dissolved in the non-aqueous solvent is not particularly limited in the present invention, and any

one of conventional ones used for non-aqueous electrolyte secondary batteries can be applied. To be specific, used may be LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$, $\text{LiB}[\text{C}_6\text{F}_3(\text{CF}_3)_2-3, 5]_4$, $\text{LiPF}_a(\text{C}_b\text{F}_{2b+1})_{6-a}$ (where a is an integer of 1 to 5 and b is an integer not smaller than 1), $\text{LiPF}_c(\text{C}_d\text{F}_{2d+1}\text{SO}_2)_{6-c}$ (where c is an integer of 1 to 5 and d is an integer not smaller than 1), $\text{LiBF}_e(\text{C}_f\text{F}_{2f+1})_{4-e}$ (where e is an integer of 1 to 3 and f is an integer not smaller than 1), $\text{LiBF}_g(\text{C}_h\text{F}_{2h+1}\text{SO}_2)_{4-g}$ (where g is an integer of 1 to 3 and h is an integer not smaller than 1).

[0017]

As the positive electrode and negative electrode of the battery using the above-described non-aqueous electrolyte, those generally used in the non-aqueous electrolyte secondary batteries of this kind are used. As the positive electrode material, a material mainly comprising a composite oxide containing lithium and one or more of transition metals (lithium-containing transition metal composite oxide) is preferable from the aspect of increasing a battery capacity and energy density. For example, suitable is an active material mainly comprising the lithium-containing transition metal composite oxide represented by the formula Li_xMO_2 (where M represents one or more of transition metals, x varies depending on the charged or discharged state of a battery, and normally $0.05 \leq x \leq 1.10$). In this Li_xMO_2 , the transition metal M is preferably at least one of Co, Ni and Mn. $\text{Li}_x\text{Mn}_2\text{O}_4$ may also be

used as the lithium-containing transition metal composite oxide, though there is no particular limitation in the present invention.

[0018]

To a negative electrode material, metal lithium and a material capable of intercalating and deintercalating lithium may be applied. The exemplary materials capable of intercalating and deintercalating lithium may include, carbon material such as a thermally decomposed carbon, cokes (pitch coke, needle coke and oil coke), graphite, a glassy carbon, a calcined matter of an organic polymer compound (obtained by calcinating a phenol resin, a furan resin or the like at a proper temperature and carbonizing it), a carbon fiber and an activated carbon, polymers such as polyacetylene, polypyrrole and polyacene, a lithium-containing transition metal oxide such as $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$, and a transition metal sulfide such as TiS_2 . The carbon material is particularly suitable among them, and, for example, when a carbon material having a structure in which the spacing between (002) lattice planes is 0.340 nm or less, namely graphite, is used, the energy density of the battery is improved.

[0019]

The positive and negative electrode materials as thus described are kneaded with, for example, a binder and a conductive agent to be processed into the electrode plate, respectively. As the binder and conductive agent to be kneaded,

any of conventionally used ones can be applied.

[0020]

The battery may be in various shapes such as cylindrical, square, coin, button, and a large type. The forms of the positive electrode and the negative electrode may be changed depending on the applied shape of the battery.

[0021]

[Examples]

(Structure of fabricated cell)

The examples of the present invention will be described as follows with reference to the drawings.

[0022]

Fig. 1 shows a vertical sectional view of a cylindrical non-aqueous electrolyte secondary battery (having a diameter of 18 mm and a total height of 65 mm) used in this example. As apparent from this figure, a band-like positive electrode plate 2 and a negative electrode plate 3 are spirally rolled up via a separator 1 to form an electrode plate assembly. A positive electrode lead plate 4 made of aluminum and a negative electrode lead plate 5 made of nickel are respectively welded to the positive electrode plate 2 and the negative electrode plate 3. A lower insulating plate 6 made of a polyethylene resin is fixed to the top and bottom of the electrode plate assembly, which is accommodated in a nickel-plated battery case 7 made of iron, and the other end of the negative electrode lead plate 5 is spot-welded to the inner

surface of the battery case 7. After an upper insulating plate 8 made of a polyethylene resin is mounted on the upper surface of the electrode plate assembly, a groove is provided in a given position close to the opening of the battery case 7, and a given amount of the non-aqueous electrolyte is poured into the battery case 7 and impregnated into the electrode plate assembly. To a lower surface of a sealing plate 10 made of stainless steel, is provided a gasket 9 made of a polypropylene resin in the circumference thereof, the other end of the positive electrode lead plate 4 is spot-welded. Then, the sealing plate 10 is fixed to the opening of the battery case 7 via the gasket 9, and the opening edge of the battery case 7 is crimped to the gasket 9 to complete the battery.

[0023]

The positive electrode plate 2 was produced in the following manner. Li_2CO_3 and Co_3O_4 were mixed and the mixture was calcinated at 900 °C for 10 hours to synthesize LiCoO_2 . 3 parts by weight of acetylene black as a conductive agent, 7 parts by weight of polytetrafluoroethylene as a binder, and 100 parts by weight of an aqueous solution containing 1 % of carboxymethyl cellulose with respect to LiCoO_2 were mixed with 100 parts by weight of LiCoO_2 . The resultant mixture was then stirred to be mixed so as to give a positive electrode material mixture paste. The positive electrode material mixture paste was applied onto both surfaces of an aluminum foil having a thickness of 30 μm serving as a current collector, dried and

rolled by pressure with a roller, and which was then cut into a predetermined size to give a positive electrode plate.

[0024]

The negative electrode plate was produced in the following manner. Flake graphite pulverized and classified to have an mean particle size of about 20 μm and 3 parts by weight of styrene/butadiene rubber as a binder were mixed, and the mixture was further added with 100 parts by weight of an aqueous solution containing 1 % of carboxymethyl cellulose with respect to the graphite. The resultant mixture was then stirred to be mixed so as to give a negative electrode material mixture paste. The negative electrode material mixture paste was applied onto both surfaces of a copper foil having a thickness of 20 μm serving as a current collector, dried and rolled by pressure with a roller, which was then cut into a predetermined size to give a negative electrode plate.

[0025]

The band-like positive electrode and negative electrode produced as described above, and a separator of a microporous film made of a polyethylene resin having a thickness of 25 μm were spirally rolled up. The non-aqueous electrolyte was prepared in each Example, which was injected and then sealed.

[0026]

(Example 1)

Using the non-aqueous electrolytes shown in (Table 1),

respectively, batteries 1 to 22 of the present invention were fabricated. (Table 1) shows the volume ratio of EMC/GBL and that of DMC/GBL of the batteries 5-12 of the present invention. VC of 2 % by volume and PC or EC of 1% by volume were contained. The concentration of the electrolyte salt was 1.25 mol/l.

[0027]

[Table 1]

	Solvent	Electrolyte salt
Battery of the invention 1	GBL+VC+PC	LiPF ₆
Battery of the invention 2	GBL+VC+PC	LiBF ₄
Battery of the invention 3	GBL+VC+EC	LiPF ₆
Battery of the invention 4	GBL+VC+EC	LiBF ₄
Battery of the invention 5	EMC/GBL(1/1)+VC+PC	LiPF ₆
Battery of the invention 6	EMC/GBL(1/1)+VC+PC	LiBF ₄
Battery of the invention 7	EMC/GBL(1/1)+VC+EC	LiPF ₆
Battery of the invention 8	EMC/GBL(1/1)+VC+EC	LiBF ₄
Battery of the invention 9	DMC/GBL(1/1)+VC+PC	LiPF ₆
Battery of the invention 10	DMC/GBL(1/1)+VC+PC	LiBF ₄
Battery of the invention 11	DMC/GBL(1/1)+VC+EC	LiPF ₆
Battery of the invention 12	DMC/GBL(1/1)+VC+EC	LiBF ₄
Battery of the invention 13	γ -valerolactone+VC+PC	LiBF ₄
Battery of the invention 14	α -acetyl- γ -butyrolactone+VC+PC	LiBF ₄
Battery of the invention 15	α -methyl- γ -butyrolactone+VC+PC	LiBF ₄
Battery of the invention 16	β -methyl- γ -butyrolactone+VC+PC	LiBF ₄
Battery of the invention 17	α -angelica lactone+VC+PC	LiBF ₄
Battery of the invention 18	α -methylene- γ -butyrolactone+VC+PC	LiBF ₄
Battery of the invention 19	γ -hexanolactone+VC+PC	LiBF ₄
Battery of the invention 20	γ -nonanolactone+VC+PC	LiBF ₄
Battery of the invention 21	γ -octanolactone+VC+PC	LiBF ₄
Battery of the invention 22	γ -methyl- γ -decanolactone+VC+PC	LiBF ₄

[0028]

(Comparative Example 1)

Comparative batteries 1 to 12 were produced using the non-aqueous electrolytes shown in (Table 2), respectively.

(Table 2) shows the volume ratio of EC/EMC of the comparative battery 2. VC of 2 % by volume and PC or EC of 1 % by volume were contained. The concentration of the electrolyte salt was 1.25 mol/l.

[0029]

[Table 2]

	Solvent (Addition ratio by volume)	Electrolyte salt
Comparative Battery 1	EC	LiPF ₆
Comparative Battery 2	EC	LiBF ₄
Comparative Battery 3	EC/EMC(1/3)	LiPF ₆
Comparative Battery 4	EC/EMC(1/3)	LiBF ₄
Comparative Battery 5	GBL	LiPF ₆
Comparative Battery 6	GBL	LiBF ₄
Comparative Battery 7	GBL+VC	LiPF ₆
Comparative Battery 8	GBL+VC	LiBF ₄
Comparative Battery 9	GBL+EC	LiPF ₆
Comparative Battery 10	GBL+EC	LiBF ₄
Comparative Battery 11	GBL+PC	LiPF ₆
Comparative Battery 12	GBL+PC	LiBF ₄

[0030]

The batteries 1 to 22 of the present invention and the comparative batteries 1 to 12 were charged and discharged at a constant current of 300 mA at an ambient temperature of 20 °C, with the final voltage for the charging of 4.1 V and the final voltage for the discharging of 3.0 V. The amount of gas generated in the batteries after the 3 cycles were measured. The results were shown in (Table 3).

[0031]

Next, the charge characteristics of the batteries under a low temperature condition were compared. The batteries were charged at a constant current and voltage under the test conditions of an ambient temperature of 20 °C, a ceiling voltage of 4.2 V, a maximum current of 1050 mA and the charging time of 2 hours and 30 minutes. Then, the charged batteries were discharged at a constant discharge current of 1500 mA at ambient temperatures of 20 °C or -20 °C until the voltage reached 3.0 V. A rate of the discharge capacity measured at -20 °C to the discharge capacity measured at 20 °C was calculated as a capacity maintenance rate under a low temperature condition.

The results were shown in (Table 3).

[0032]

After the charged batteries were stood still at a temperature of 85 °C for 72 hours, the discharge characteristics of the batteries were compared. The batteries were charged at a constant current and voltage under the test conditions of an ambient temperature of 20 °C, a ceiling voltage of 4.2 V, a

maximum current of 1050 mA and the charging time of 2 hours and 30 minutes. Then, the charged batteries were discharged at a constant discharge current of 1500 mV at an ambient temperature of 20 °C until the voltage reached 3.0 V. The discharge capacities of the batteries at 20 °C were measured before and after the batteries were stood still at 85 °C, and a rate of the discharge capacity after the battery was stood still to that before the battery was stood still was calculated as a capacity maintenance rate. The results were shown in (Table 3).

[0033]

[Table 3]

	Gas amount (ml)	Capacity maintenance rate under a low temperature condition (%)	Capacity maintenance rate after storage at a high temperature (%)
Battery of the invention 1	1.2	75	87
Battery of the invention 2	1.3	73	84
Battery of the invention 3	1.1	71	85
Battery of the invention 4	1.3	70	85
Battery of the invention 5	1.5	78	89
Battery of the invention 6	1.6	76	87
Battery of the invention 7	1.6	78	86
Battery of the invention 8	1.7	76	86
Battery of the invention 9	1.9	80	89
Battery of the invention 10	1.8	79	88
Battery of the invention 11	1.9	78	88
Battery of the invention 12	1.7	72	89
Battery of the invention 13	1.6	73	83
Battery of the invention 14	1.4	70	82
Battery of the invention 15	1.7	73	84
Battery of the invention 16	1.4	71	80
Battery of the invention 17	1.3	74	81
Battery of the invention 18	1.8	72	82
Battery of the invention 19	1.5	75	82
Battery of the invention 20	1.3	71	83
Battery of the invention 21	1.7	73	81
Battery of the invention 22	1.4	72	80

[Table 3-continued]

Comparative Battery 1	1.6	Electrolyte froze at -20°C	65
Comparative Battery 2	1.7	Electrolyte froze at -20°C	60
Comparative Battery 3	3.8	35	79
Comparative Battery 4	3.9	32	67
Comparative Battery 5	21.0	25	5
Comparative Battery 6	28.0	22	5
Comparative Battery 7	1.8	72	34
Comparative Battery 8	1.9	70	35
Comparative Battery 9	16.0	31	7
Comparative Battery 10	18.0	30	7
Comparative Battery 11	19.0	19	4
Comparative Battery 12	17.0	16	5

[0034]

As shown in (Table 3), in the comparative batteries 5 and 6, a great amount of decomposition gas was observed as a result of decomposition of GBL on the negative electrode. Also in the comparative batteries 9 to 12, a great amount of decomposition gas was observed, indicating that PC or EC formed a film on the negative electrode so slowly that the decomposition of GBL at the negative electrode was not sufficiently suppressed. In the batteries 1 to 22 of the present invention, in comparison, it is considered that VC so rapidly formed a film derived from a decomposed product on the negative electrode that the decomposition of GBL and a lactone-

type solvent at the negative electrode was sufficiently suppressed, greatly decreasing the amount of decomposition gas.

[0035]

The comparative batteries 1 and 2 shown in (Table 3) were totally unable to be discharged at -20°C since EC froze at the low temperature. Also in the comparative batteries 3 and 4 where EC and EMC were contained, the capacity maintenance rate under a low temperature condition was as low as 35%, although the electrolyte did not freeze at -20°C. On the other hand, the batteries 1 to 22 of the present invention had highly excellent capacity maintenance rates under a low temperature condition, attributed to the very low solidifying points of GBL and the lactone-type solvent.

[0036]

When the comparative batteries 7 and 8 shown in (Table 3) were stood still under a high temperature condition over a period of time, the polymerization reaction of VC on the negative electrode was accelerated to form an excessive film on the negative electrode. As a result, lithium ions are not smoothly intercalated into and deintercalated from the negative electrode, causing a very low capacity maintenance rate after storage at a high temperature. The batteries 1-4 and 13-22 of the present invention, in comparison, has highly excellent capacity maintenance rates after storage at a high temperature since EC or PC suppresses the polymerization reaction of VC at a high temperature condition. Furthermore, it was found that

containment of a linear carbonic acid ester such as EMC or DMC in the non-aqueous electrolyte, as done in the batteries 5 to 12 of the present invention, was effective to decrease the viscosity of the non-aqueous electrolyte so as to further improve the capacity maintenance rate under a low temperature condition.

[0037]

It was found from the above results that a non-aqueous electrolyte secondary battery, having excellent charge and discharge characteristics at a low temperature and showing satisfactory charge and discharge characteristics even after exposure to a high temperature over a period of time, can be realized by using an electrolyte dissolving a solute in a non-aqueous solvent comprising a cyclic carboxylic acid ester, a cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond and a cyclic carbonic acid ester having no unsaturated bond.

[0038]

(Example 2)

Because of extremely rapid polymerization reaction of VC on the negative electrode, addition of an excessive amount of VC possibly causes the formation of an excessive film, which deteriorates the low temperature characteristics. The content of VC was therefore studied. GBL as the cyclic carboxylic acid ester, PC (1 % by volume) as the cyclic carbonic acid ester having no unsaturated bond and LiBF₄ (1.25 mol/l) as the

electrolyte salt were used and the VC content was varied to perform a comparison of the discharge characteristics under a low temperature condition. The results were shown in Table 4. The test conditions are the same as those of Example 1.

[0039]

[Table 4]

VC content (vol %)	Capacity maintenance rate under a low temperature condition (%)
0.1	Unable to be charged and discharged
0.5	61
1	71
5	72
10	65
20	60
30	42

[0040]

As shown in (Table 4), not enough film was formed to suppress the reductive decomposition of GBL when the addition ratio of VC was 0.1% by volume, and the charge and discharge reaction did not proceed sufficiently even at an ordinary temperature. When the addition ratio of VC was 30% by volume, a film was excessively formed on the negative electrode due to the reductive decomposition of VC, thereby decreasing the capacity maintenance rate at a low temperature. Accordingly, the appropriate addition amount of VC is 0.5-20 % by volume, with satisfactory low temperature characteristics were exhibited.

[0041]

(Example 3)

Next, the contents of PC and EC were studied. Using GBL as the cyclic carboxylic acid ester, VC (2 % by volume) as the cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond and LiBF₄ (1.25 mol/l) as the electrolyte salt and varying the contents of PC and EC, the discharge characteristics under a low temperature condition were compared, and the discharge characteristics after storage at 85°C for 72 hours were also compared. The results were shown in (Table 5). The test conditions are the same as those of Example 1.

[0042]

[Table 5]

PC or EC Content	Capacity maintenance rate under a low temperature condition (%)	Capacity maintenance rate after storage at a high temperature (%)
PC (0.1 vol%)	74	72
PC (0.5 vol%)	73	77
PC (1 vol%)	73	84
PC (5 vol%)	72	85
PC (10 vol%)	70	81
PC (20 vol%)	65	78
PC (30 vol%)	51	75
EC (0.1 vol%)	72	70
EC (0.5 vol%)	72	79
EC (1 vol%)	70	85
EC (5 vol%)	69	84
EC (10 vol%)	68	80
EC (20 vol%)	65	78
EC (30 vol%)	51	74

[0043]

As shown in (Table 5), relatively good capacity maintenance rates after storage at a high temperature were obtained even when the content of PC or EC was 0.1% by volume. When the content of PC or EC was 30% by volume, the capacity maintenance rate after storage at a high temperature decreased only slightly, but the capacity maintenance rate under a low temperature condition deteriorated considerably. This is presumably because the conductivity at a low temperature decreased if the content of PC or EC became large, and the capacity maintenance rate also dropped. It was found from these results that the content of PC or EC is suitably from 0.1-20 % by volume.

[0044]

In the present examples, only a few of compounds were described in terms of the cyclic carboxylic acid esters, cyclic carbonic acid esters having carbon-carbon unsaturated bond, and cyclic carbonic acid esters having no unsaturated bond. However, it should be noted that other compounds have had similar effects, and therefore, the present invention is not limited to the examples thus described.

[0045]

[Effect of the Invention]

As described above, the present invention is characterized in use of an electrolyte dissolving a solute in a non-aqueous solvent comprising the cyclic carboxylic acid ester, the cyclic carbonic acid ester having at least one carbon-

carbon unsaturated bond and the cyclic carbonic acid ester having no unsaturated bond. The cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond allows suppressing the reductive decomposition of the cyclic carboxylic acid ester on the negative electrode by forming a close and strong film on the negative electrode. When the battery is exposed to a high temperature over a period of time, the cyclic carbonic acid ester having at least one carbon-carbon unsaturated bond excessively forms a film on the negative electrode, but the cyclic carbonic acid ester having no unsaturated bond suppresses the excessive formation of the film. As a result, a non-aqueous electrolyte secondary battery, having excellent charge and discharge characteristics at a low temperature and showing satisfactory charge and discharge characteristics even after the battery is stood still under a high temperature condition over a period of time, can be realized.

[BRIEF EXPLANATION OF THE DRAWINGS]

[FIG. 1]

A vertical sectional view of the cylindrical lithium-ion secondary battery used in the examples of the present invention.

[Explanation of Reference Numerals]

- 1 Separator
- 2 Positive electrode plate
- 3 Negative electrode plate

- 4 Positive electrode lead plate
- 5 Negative electrode lead plate
- 6 Lower insulating plate
- 7 Battery case
- 8 Upper insulating plate
- 9 Gasket
- 10 Sealing plate

【書類名】 図面 [DOCUMENT NAME] Drawing

【図1】 [FIG. 1]

